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Novel MK2266A antibiotic - active against *Micrococcus luteus*, *E*
Escherichia coli, *candida albicans* etc.

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Abstract (Basic): JP 6211617 A

Antibiotic MK2266A having m.pt. of 173-174 deg.C physiochemical props defined in the specification of formula (I) is new.

Dactylaria sp. esp. dactylaria parvispora D500 (FERM P-12798) is aerobically cultured in a conventional medium at 10-30, (pref. 20-27) deg.C for 3-10 days and MK2266A is isolated and purified by known methods.

USE/ADVANTAGE - MK2266A is active against microorganisms. including bacteria, fungi and yeasts.

In an example, MK2266A exhibited antimicrobial activity, against *micrococcus luteus* ATCC 9431, *escherichia coli* NIHJ, *candida albicans* M9001, *cryptococcus neoformans* M9010, and *hansenula schneggi* IAM 4269 with MIC values of 7100, 7100, 7100, 6.2 and 100 ug/ml resp.

Dwg.0/0

Derwent Class: B03; C02; D16

International Patent Class (Main): A01N-063/04

International Patent Class (Additional): C07D-309/36; C12P-017/06;

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SPECIFICATION

1. TITLE OF THE INVENTION

PROCESS FOR PRODUCING MICROPOROUS MEMBRANE

2. CLAIM

A process for producing a microporous membrane, comprising casting on a support a membrane-forming stock solution in which a polymer is dissolved in a solvent, and then immersing the support in a coagulating bath, characterized in that two or more coating layers are provided on the support by simultaneously or successively casting two or more membrane-forming stock solutions as the membrane-forming stock solutions, and then the support is immersed and coagulated in the coagulating bath.

3. DETAILED DESCRIPTION OF THE INVENTION

<Field of the Invention>

The present invention relates to a process for producing a microporous membrane. More particularly, the present invention relates to a process for producing a microporous membrane having a multi-layered structure.

<Conventional Art>

Microporous membranes have been known for a long time (for example, R. Kesting, Synthetic Polymer Membrane, McGraw-Hill Book Company, Inc.), and widely used for filters for filtration and the like. Microporous membranes include, for example, ones which are produced from cellulose esters as raw materials as described in U.S. Patent Nos. 1,421,341, 3,133,132, and 2,944,017, and Japanese Patent Publication Nos. 43-15698, 45-33313, 48-39586

and 48-40050, ones which are produced from aliphatic polyamides as raw materials as described in U.S. Patent Nos. 2,783,894, 3,408,315, 4,340,479, 4,340,480 and 4,450,126, German Patent No. 3,138,525, and Japanese Patent Laid-Open No. 58-37842, ones which are produced from polyfluorocarbons as raw materials as described in U.S. Patent Nos. 4,196,070 and 4,340,482, and Japanese Patent Laid-Open Nos. 55-99934 and 58-91732, ones which use polysulfones as raw materials as described in Japanese Patent Laid-Open Nos. 56-154051, 56-86941 and 56-12640, and ones which use polypropylenes as raw materials as described in German Patent No. OLS3,003,400. These microporous membranes are used for filtration and sterilization of washing water for electronic industries, water for pharmaceuticals, water for production processes of pharmaceuticals, water for foods and the like, and the applications and use amount have recently been expanded. Highly reliable microporous membranes are focused on and much used especially from the viewpoint of particle capturing.

<Problems to be Solved by the Invention>

However, the membranes produced by the above conventional arts are ones whose polymer components are single, or composite membranes using quite limited blendable polymers. For example, a polyurethane-polyepoxide-based blend (J. Appl. P. S., 25, 1105(1980)), and a blend membrane of an aromatic polysulfone and an aromatic polyether sulfone, described in Japanese Patent Laid-Open No. 56-86941, are known.

However, such a blend membrane cannot exhibit the property of each polymer as it is, and then exhibit no more than the nearly same performance as that of a single polymer membrane.

On the other hand, for example, as in a case where an ethanol aqueous solution of a polyvinylalcohol-polystyrene sulfonic acid is cast on a polypropylene porous membrane (J. Appl. P. S., 27, 2783(1982)), a process is known in which another membrane is newly formed by newly coating on a previously formed membrane to fabricate a microporous composite membrane. However, coating on a previously formed membrane as in this case does not have a processing merit, and is not preferable as well since the resistance against permeability becomes large corresponding to the volume of the support. Adhesiveness of membranes themselves is not

sufficient and often not practical. Since, for improving the adhesiveness, a solvent capable of dissolving the surface of an already existing membrane is used, and a highly compatible polymer solution must be coated, the influence of the coating solvent on the first membrane cannot be avoided on coating the second layer, resulting in drawbacks such as damage to the membrane uniformity.

As the result of extensive studies to solve such conventional drawbacks, the present inventors have found that if membrane-forming stock solutions are simultaneously or successively cast, a specific microporous membrane substantially integrated and having a multi-layered structure, which cannot be conventionally obtained, can be obtained, and achieved the present invention.

Accordingly, a first object of the present invention is to provide a process for producing a microporous membrane which is substantially integrated and never exfoliates, and has a multi-layer structure.

A second object of the present invention is to provide a process for producing a microporous membrane in which two or more layers of polymer membranes having different pore sizes are substantially integrated.

A third object of the present invention is further to provide a process for producing a multi-functional microporous membrane in which a microporous membrane and a membrane having a function different from a common microporous membrane are made to have a multi-layered structure, and substantially integrated.

<Means for Solving the Problems>

The above objects of the present invention are achieved by a process for producing a microporous membrane, comprising casting on a support a membrane-forming stock solution in which a polymer is dissolved in an organic solvent, and then immersing the support in a coagulating bath, characterized in that two or more layers are provided on the support by simultaneously or successively casting two or more membrane-forming stock solutions as the membrane-forming stock solutions, and the support is immersed and coagulated in the

coagulating bath. As the membrane-forming stock solutions used in the present invention, those optionally selected from membrane-forming stock solutions commonly used for producing microporous membranes are usable. Therefore, the membrane-forming stock solutions in the present invention include not only a membrane-forming stock solution in which a polymer as a single substance, represented by cellulose ester, polyamide, polyimide, polysulfone, polyvinylidene halide, polycarbonate, polystyrene, polyacrylnitrile, polyarylhydrazide and the like, is dissolved in a suitable solvent, but also a membrane-forming stock solution in which two or more polymers are blended as in the case of blending of, for example, polysulfone and polyethylene glycol. For preparing these membrane-forming stock solutions, conventionally known arts can be suitably used.

In production of a microporous membrane, the above polymer is dissolved in a solvent, (1) a good solvent, (2) a mixed solvent of a good solvent and a nonsolvent, or (3) a mixed solvent of a plurality kinds of solvents having different solubilities of the polymer, to fabricate a membrane-forming stock solution, which is cast on a support or directly in a coagulating bath, washed, and dried. In this case, the solvent dissolving the polymer includes, for example, chloromethane, acetone, dimethylformamide, dimethylacetamide, dimethylsulfoxide, 2-pyrrolidone, N-methyl-2-pyrrolidone, sulfolane and hexamethylphosphoramide.

The nonsolvent added to the above solvent includes, for example, water, cellosolves, methanol, ethanol, propanol, acetone, tetrahydrofuran, polyethylene glycol and glycerol. The ratio of a nonsolvent to a good solvent can be within any range to keep the mixed solvent homogeneous, but is preferably 5% by weight to 50% by weight.

A substance to control the porous structure, referred to as a swelling agent, such as an inorganic electrolyte, organic electrolyte, polymer or an electrolyte thereof, can be added.

Used as the electrolyte in the present invention is a metal salt of an inorganic acid such as common salt, sodium nitrate, potassium nitrate, sodium sulfate or zinc chloride, a metal salt of an organic acid such as sodium acetate or sodium formate, a polymer electrolyte such as a sodium polystyrenesulfonate or polyvinylbenzyltrimethylammonium chloride, a polymer such as a polyvinylpyrrolidone, and an ionic surfactant such as sodium dioctylsulfosuccinate or a sodium

alkylmethyltaurate. These electrolytes exhibit an effect of some degree even by adding them alone to a polymer solution, but exhibit a particularly remarkable effect when they are added as an aqueous solution. The adding amount of the electrolyte aqueous solution is not specifically limited as long as the homogeneity of the solution is not lost by the addition, but is commonly 0.5% by volume to 10% by volume to the solvent. The concentration of the electrolyte aqueous solution also is not specifically limited, and the larger concentration has a larger effect, but the commonly used concentration is 1% by weight to 60% by weight. The concentration of a polymer solution as a membrane-forming stock solution is 5 to 35% by weight, preferably 10 to 30% by weight. With the concentration exceeding 35% by weight, the water permeability of an obtained microporous membrane becomes as low as having no practical significance. By contrast, with that not more than 5% by weight, a microporous membrane having a sufficient separation capability cannot be obtained.

"Two or more membrane-forming stock solutions" in the present invention notionally include of course a case where the polymer components dissolved in stock solutions are different, a case where the same polymer components are dissolved in different solvents, and further a case where although the polymer components and the solvents respectively are the same, the polymer concentrations in stock solutions are different, but especially the case where the kinds of polymers are different is a preferable embodiment of the present invention since a microporous composite membrane conventionally not obtained can be obtained.

As the casting techniques employed in the present invention, well-known arts can be suitably combined and used, but the so-called extrusion to extrude a membrane-forming stock solution from a slit is especially preferable, and with a plurality of slits, easily allows simultaneous multi-layered casting.

These casting techniques employable in the present invention are described, for example, in Soc. of Photographic Science and Technology, Japan, editor, "Fundamentals of Photographic Engineering", p. 255 to p. 257.

In the present invention, generally a support base is used, and membrane-forming stock solutions are cast on the support base. However, without using the support base,

membrane-forming stock solutions can also be cast directly from a casting die into a coagulating bath. In either case, the so-called interdiffusion phenomenon occurs in which the solvents of the polymers diffuse from layered membrane-forming stock solutions into the coagulation solution while a nonsolvent in the coagulation solution diffuses and penetrates into the membrane-forming stock solutions, whereby the polymers deposit, and a membrane having micropores is formed.

That is, the coagulating bath used in the present invention has as the main component a nonsolvent for a polymer to be used, and is one which can deposit and precipitate the polymer. Therefore, the solution composition of the coagulating bath is adjusted so that the inflow of the membrane-forming stock solution does not largely change it. The solution composition and temperature of the coagulating bath can suitably be selected depending on the polymer kind, the properties of a membrane formed by the polymer deposition (such as, symmetrical structure or asymmetrical structure), and the like. As a coagulation solution in the coagulating bath, water is most commonly used, but an organic solvent not to dissolve a polymer, or a mixture of two or more these nonsolvents can be used.

<Operation>

Since the process of the present invention forms a multi-layered structure in the state of a stock solution, not only diffusion of the solvents between each layer, but also entanglement of the polymers between each layer occurs. By way of such a state, membrane formation of polymers is performed in a coagulating bath; therefore the layers after membrane formation have a good affinity with each other; and then a microporous membrane substantially integrated can be obtained though assuming a multi-layered structure. In particular, in the case of using two or more different kinds of polymers, which are even a combination of polymers inferior in compatibility which cannot be used in the blending method, the adhesiveness between layers is sufficient, causing no anxiety about exfoliation in practical use. Further, different from the conventional blending, this method does not only make the best use of the merits of each polymer, but also can add different functions. For example, if a polymer having ion exchange

capability is used for one of the polymers to be used, a microporous membrane having ion exchange capability can even be produced. In this case, if a flexible polymer is used for another of the polymers, postprocessing such as pleating is well allowed. Similarly, a microporous membrane having several enzyme-containing layers can also be easily produced. Further, when membranes having larger pores are formed on both sides of a membrane having smallest pores, reliability is also more improved as a microporous membrane having little influence when the membrane is flawed.

<Advantages of the Invention>

According to the production process of the present invention, a microporous membrane designed in advance can be easily produced by using an optional polymer and making the best use of inherent properties of each polymer. Since the membrane obtained by the process of the present invention has an excellent affinity between layers of the multilayer structure, and can be said to have an integrated structure, it can well withstand a necessary postprocessing such as pleating. Besides, when a so-called functional polymer is used as a polymer to be used, a multi-functional microporous membrane can also be obtained.

Hereinafter, the present invention will be explained further in detail by way of examples, but the present invention is not limited by them.

Example 1

Next two kinds of membrane-forming stock solutions were prepared using a polysulfone P-3500 (manufactured by UCC Corp.), N-methyl-2-pyrrolidone (NMP) and a polyethylene glycol (PEG) having a molecular weight of 4,000. Here, % denotes % by weight.

(A) polysulfone	(10%)
NMP	(80%)
PEG 4000	(10%)
(B) polysulfone	(20%)
NMP	(80%)

On a polyethylene terephthalate (PET) base, (A) was cast in a thickness of 100 μm ; (B) was cast thereon in a thickness of 3 μm , and immediately immersed in a coagulation solution of water/N-methyl-2-pyrrolidone of 1/2 to obtain a microporous membrane.

The pore size was 0.03 μm ; and the water permeability was 4 $\text{ml}/\text{cm}^2 \cdot \text{min} \cdot \text{atm}$.

For comparison, samples of (A) alone cast and coagulated in a thickness of 103 μm and (B) alone cast and coagulated in a thickness of 103 μm were fabricated.

The water permeability of a membrane obtained from (A) alone was as large as 20 $\text{ml}/\text{cm}^2 \cdot \text{min} \cdot \text{atm}$, and the pore size was also as large as 0.2 μm ; on the other hand, the pore size of a membrane obtained from (B) alone was as small as 0.03 μm , but the water permeability was as very small as 0.08 ml . Either case was verified to be remarkably inferior in performance to a membrane obtained in the present invention.

Example 2

Membrane-forming stock solutions of the compositions below were prepared using a polyvinylidene fluoride resin (PVdF), manufactured by Penwalt Corp., dimethylacetamide (DMAc) as a solvent, and a polyethylene glycol (PEG) of 4,000 in molecular weight as an additive.

- (A) PVdF (5%), DMAc (85%), PEG (10%)
- (B) PVdF (30%), DMAc (60%), PEG (10%)
- (C) PVdF (8%), DMAc (82%), PEG (10%)

On a PET, membrane-forming stock solutions with C solution of 50 μm , B solution of 2 μm thereon, and A solution of 50 μm on the most upper layer, were cast from a triple casting die, and immediately immersed and coagulated in methanol of 30°C to obtain a microporous membrane. This membrane was a two-side asymmetric membrane having a dense micropore layer inside the membrane, and was clarified to be a microporous membrane hardly susceptible to an influence such as external damage.

Example 3

Two kinds of membrane-forming stock solutions below were prepared.

(A) polysulfone	(10%)
NMP	(80%)
PEG 1000	(10%)
(B) sulfonated polysulfone	(6%)
NMP	(80%)
PEG 1000	(10%)

On a PET support, B solution was cast in a thickness of 400 μm ; A solution was cast thereon in a thickness of 100 μm , and immediately put and coagulated in water of 20°C. The obtained membrane was a membrane integrated of an ion exchange membrane of the sulfonated polysulfone and a polysulfone microporous filter membrane, and had a filtration rate of 120 $\text{ml}/\text{cm}^2 \cdot \text{min} \cdot \text{atm}$, a pore size of 0.4 μm and an ion exchange capability of 20 meq/cm^2 .

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